

COAL PYROLYSIS: MEASUREMENTS AND MODELING OF PRODUCT EVOLUTION KINETICS AND CHAR PROPERTIES

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INTRODUCTION

Thermogravimetric analysis (TGA) has been employed in coal science to perform a number of characterizations including: proximate analysis,¹ kinetics of weight loss,² char reactivity,³⁻⁶ and gas adsorption measurements.⁷ A complementary technique, evolved product analysis, has been employed to study pyrolysis product distributions and kinetics,⁸⁻¹¹ functional group compositions,^{10,12,13} and temperature programmed desorption.¹⁴⁻¹⁵ We have developed a TG-FTIR instrument which combines TGA with evolved product analysis by Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR analysis of evolved products has advantages over mass spectroscopy in allowing analysis of very heavy products, and over gas chromatography in speed.

The application of TG-FTIR to coal and petroleum source rock has recently been described.^{16,17} To analyze coal, a sequence of drying, pyrolysis and combustion is employed to obtain: proximate analysis, volatiles composition, volatiles kinetics, and relative char reactivity. By using several different heating rates, kinetic rate constants have been obtained.^{18,19} The purpose of this paper is to describe its application in characterizing the volatile evolution kinetics and char reactivities of the Argonne premium coal samples. The technique is being employed to obtain the kinetic and composition parameters for a recently developed general model of coal pyrolysis, called the FG-DVC model,²⁰ which stands for Functional Group - Depolymerization, Vaporization and Crosslinking model. This is a network model based on an assumed polymeric structure for coal and includes the processes of depolymerization and crosslinking and the formation of char, tar and gases. The reactivity parameters will be included in an extension of the model which is currently under development.

EXPERIMENTAL

Apparatus - A schematic of the TG-FTIR instrument is presented in Fig. 1. Its components are as follows: a DuPont 951 TGA; a hardware interface (including a furnace power supply); an Infrared Analysis 16 pass gas cell with transfer optics; a MICHELSON 110 FT-IR; (Resolution: 4 cm⁻¹, Detector: MCT). A helium sweep gas (250 cc/sec) is employed to bring evolved products from the TGA directly into the gas cell. A window purge of 700 cc/sec is employed at each end of the cell. The system is operated at atmospheric pressure. This instrument package is now available commercially as the "TG/plus" from Bomem, Inc.

The most difficult volatiles to analyze are the heavy decomposition products which condense at room temperature, such as tars from coal. In the TG/plus, the high conductivity helium sweep gas and the rapid cooling cause these products to form an aerosol which is fine enough to follow the gas through the analysis cell. The cell is connected without restrictions to the sample area. The aerosol is also fine enough that there is only a little scattering of the infrared beam and it is thus attenuated almost as though the tar was in the gas phase, as shown in Fig. 2. Based on the aerosol's Rayleigh scattering of infrared radiation, the diameter of the aerosol droplets is less than 1.0 μm .

Procedure - As an example of the analysis procedure, the pyrolysis and oxidation of a lignite is described. More detail can be found in Refs. 16 - 18. Figure 3a illustrates the weight loss from

this sample and the temperature history. A 35 mg sample of Zap lignite, loaded in the sample basket of the DuPont 951, is taken on a 30°C/min temperature excursion in the helium sweep gas, first to 150°C to dry for 240 sec, then at 30°C/min to 900°C for pyrolysis. Upon reaching 900°C, the sample is immediately cooled to 250°C over a twenty minute period. After cooling, a small flow of O₂ (0.3 cc/sec) is added to the helium sweep gas at the 57 minute mark and the temperature is ramped to 700°C at 30°C/min (or as high as 1000°C) for oxidation.

During this excursion, infrared spectra are obtained once every thirty seconds. As shown in Fig. 2, the spectra show absorption bands for CO, CO₂, CH₄, H₂O, SO₂, COS, C₂H₄, and NH₃. The spectra above 250°C also show aliphatic, aromatic, hydroxyl, carbonyl and ether bands from tar. The evolution of gases derived from the IR absorbance spectra are obtained by a quantitative analysis program which employs a database of integration regions and calibration spectra for different compounds¹⁶⁻¹⁸. The routine employs regions of each calibration spectrum which permit the best quantitation with the least interferences. The routine is fast enough to allow the product analysis to be displayed on the computer screen during the actual experiment.

Figure 3b illustrates the integral of the evolution curves to obtain cumulative evolved product amounts. Because the data are quantitative, the sum of these curves match the weight loss as determined by the H₂ balance. Discrepancies occur in this match because of missing components such as H₂ which cannot be seen by IR. Also, when O₂ is introduced, the balance shows a net gain in weight due to O₂ chemisorption.

Reactivity Measurements - Initial char reactivity measurements were made using the isothermal measurement developed at Pennsylvania State University in which the time for 50% burnoff ($\tau_{0.5}$) was measured.⁶ In our char characterization work, we had difficulty applying the isothermal technique to chars formed over a wide range of conditions. A temperature level selected for one char was inappropriate for another. The temperature was either too high for the rate to be chemically controlled or too low for the $\tau_{0.5}$ to be reached in a reasonable time period.

In order to overcome this difficulty, a non-isothermal technique was developed.^{3,5} A Perkin-Elmer TGA 2 was initially used for this method. Recent measurements have been made using the TG-FTIR instrument discussed above and good agreement has been found between these two systems. The sample is heated in air at a rate of 30 K/min until a temperature of 900°C is reached. The TGA records the sample weight continuously and, at the end of the experiment, the weight and derivative are plotted.

The "critical" temperature (T_{cr}) at which the derivative of the fractional weight loss with respect to time reaches a value of 0.065 wt. fraction/min = 0.001 wt. fraction/s was chosen as an index of reactivity to be compared with the $\tau_{0.5}$ values measured by the isothermal technique. The actual critical slope used is arbitrary. A value is chosen which is large enough to be unambiguously determined, but small enough so that reaction occurs in the chemically controlled regime. Values of $\ln \tau_{0.5}$ were plotted against $1/T_{cr}$ and a good correlation was observed.³

Temperature Programmed Desorption - Temperature programmed desorption (TPD) has proved to be a valuable tool for characterization of surfaces of carbonaceous materials such as coal chars.^{14,15} An example of the application of this technique to the characterization of chars from two coals is shown in Figure 4. This work was done in our TG-FTIR system described above by operation in a slightly different mode. The chars were prepared by programmed pyrolysis at 30° C/min to 1000° C, then cooled to 200° C, exposed to air for ten minutes, and then reheated to 1000° C. Samples which have a high oxidation reactivity have a larger increase in weight due to O₂ uptake and desorb CO₂ much more readily. In Figure 4, a comparison is made between a highly reactive char produced from a low rank (Zap lignite) coal (solid line) compared with a relatively unreactive char produced from a high rank (Pocahontas) coal (dashed line). The differences between these samples can be rapidly and easily assessed using this technique.

Samples - The coals analyzed were Argonne premium coal samples. The characterization of these samples has appeared elsewhere.²¹

RESULTS

Char Properties - The results from the application of the TG-FTIR instrument to measurements of T_g and oxygen chemisorption capacity on the Argonne Premium coals are shown in Fig. 5. As expected, the values of T_g decrease with decreasing rank which indicates that lower rank coals are more reactive. This variation in reactivity with rank is primarily due to mineral contributions to reactivity.^{3,5} The measurements of oxygen chemisorption capacity (OCC), which are related to the active site concentration, are inversely related to T_g and are also shown in Fig. 5. In our work, we have found that the value of T_g is a more useful correlative parameter for reactivity than the OCC.²²

Kinetics - The TG-FTIR system was used to conduct programmed pyrolysis experiments on the Argonne premium coals over a range of heating rates (3, 30, 50, 100°C/min).^{18,19} When comparing the multi-peak evolution curves of a given specie in different coals, an interesting feature was observed. As the coal is increased in rank, the leading edges and the early peaks shift to higher temperatures while the trailing edges remain at the same temperature. An example of this is shown for water for five coals in Fig. 6.²³ From this figure it appears that this feature can be explained in the light of the geological aging process of coal formation. With increasing aging temperature and time, the maturation process gradually evolves the loosely bound functional groups and leaves the tightly bound groups intact. The FG-DVC model has been used to successfully simulate the shifts in the evolution curves as a function of rank.²³ This was done by extrapolating the kinetics determined in the TG-FTIR experiments at moderate heating rates (3-100°C/min) to geological conditions and assuming that the coals of increasing rank are the products from lower rank coals pyrolyzed under natural conditions at increased times and temperatures.

Relationships between Kinetic Rates of Different Volatile Species - It was also found that some pools in the different gas species have peak evolution rates at the same temperature and those peaks have the same shifts when the heating rate changes. The Utah Blind Canyon coal gives a good example as shown in Fig. 7. The TG-FTIR measurements indicate that the tar evolution, the CO₂-Loose, CO-Loose, and the H₂O-Loose pools all show very close peak temperatures at about 480° C for 30° C/min., at about 519° C for 100° C/min. and at about 430° C for 3° C/min. runs. This feature implies that these volatile pools can be fit with the same kinetic parameters. This may also imply that there is some common chemistry.

Model Predictions - The kinetic parameters for the functional group pools from the eight Argonne premium coals have been determined using a set of rules that were developed to allow a systematic method of establishing the rank variations (e.g., the frequency factors were fixed at values of less than 10¹⁵/sec. and only the activation energies were allowed to vary with rank). The details will be provided in a future publication. A typical comparison of theory and TG-FTIR experiments is shown in Figs. 8 and 9 for two widely spaced heating rates. The agreement between the theory and experiment is generally quite good except for CO₂. For this specie, residual oxygen in the TG-FTIR causes some oxidation at the slowest heating rate and minerals contribute evolved CO₂ which is not modeled. CO also shows some differences in the predicted amplitude, while the agreement is good for water, weight-loss, CH₄, tar and H₂O. The kinetic parameters obtained from the TG-FTIR method extrapolate well to very low heating rates, as in natural maturation processes,²³ as well as to the high heating rates of importance in most coal gasification and combustion processes.¹⁹

CONCLUSIONS

The TG-FTIR instrument provides a simple, fast and reliable method for providing information on product evolution kinetics and char reactivity for coals and other polymeric materials. The information from this test has been used to provide validated kinetic and composition

parameters for a general model of coal pyrolysis, called the FG-DVC model. This model can make accurate predictions of both very low and very high heating rate pyrolysis events.

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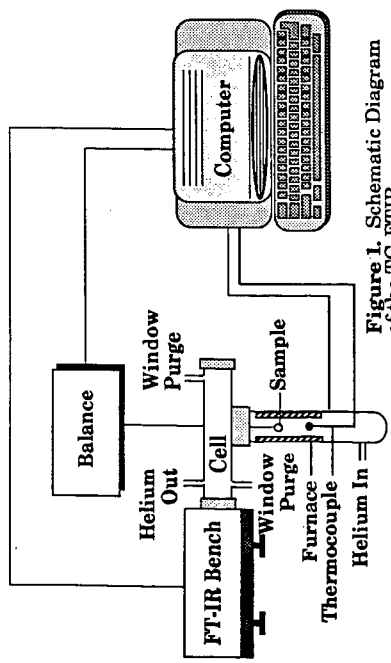


Figure 1. Schematic Diagram of the TG-FTIR.

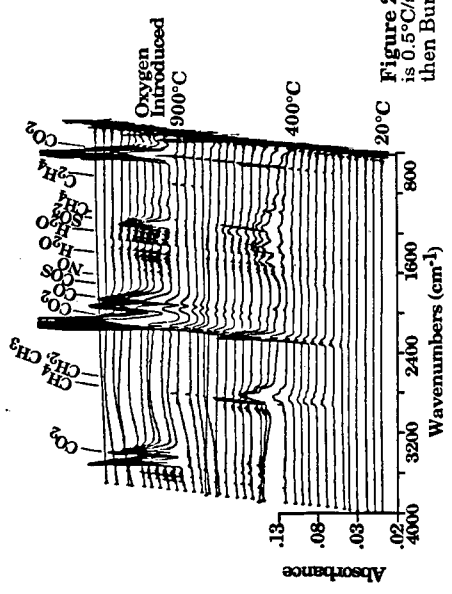


Figure 2. Spectra from TG-FTIR of Coal. Heating Rate is 0.5°C/s⁻¹ from 20 to 900°C. The Remaining Char is then Burned at 700°C.

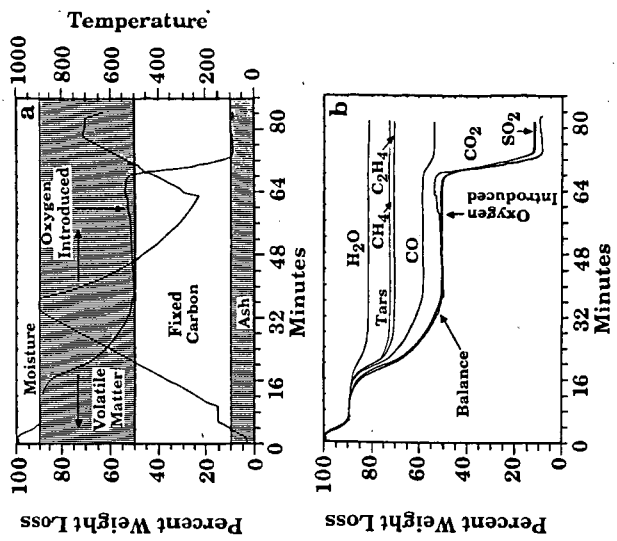


Figure 3. TG-FTIR Analysis of a Lignite. a) Temperature History and Weight Loss; b) Species Contributions to Weight Loss.

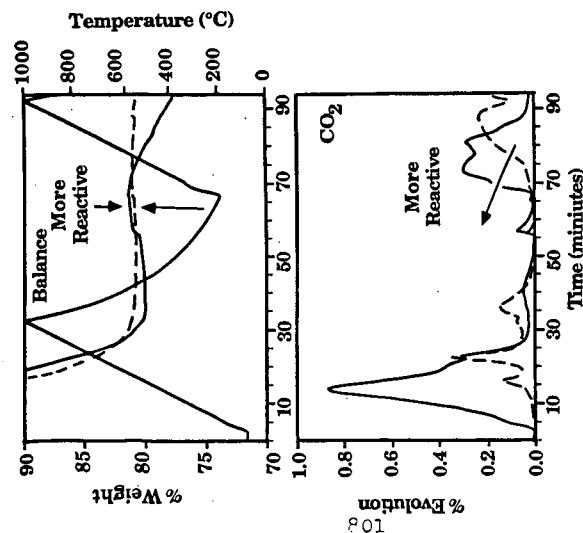


Figure 4. Temperature Programmed Desorption Curves for Pocahontas (---) and Zap Lignite (—).

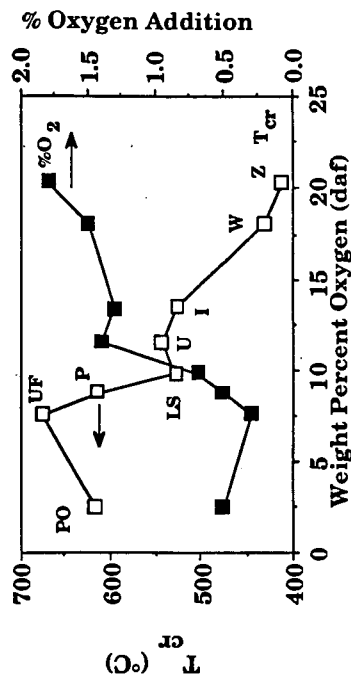


Figure 5. Rank Variation of T_{cr} and Oxygen Chemisorption Capacity (as-received basis).

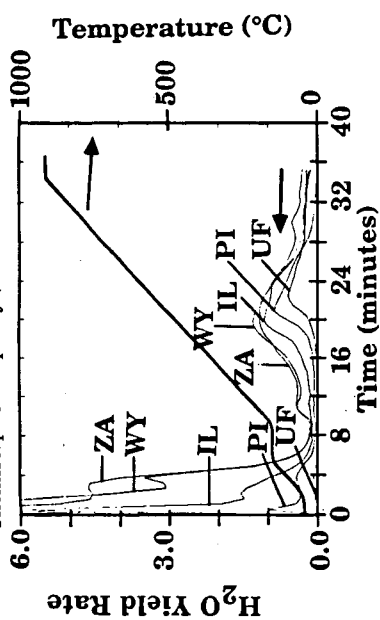


Figure 6. Evolution Curves for H_2O Measured in a TG/Plus for Five Coals from the Argonne Premium Samples Collected at $30^\circ C/min$ (UF: Upper Freeport, PI: Pittsburgh, IL: Illinois, WY: Wyodak, ZA: Zap Lignite)

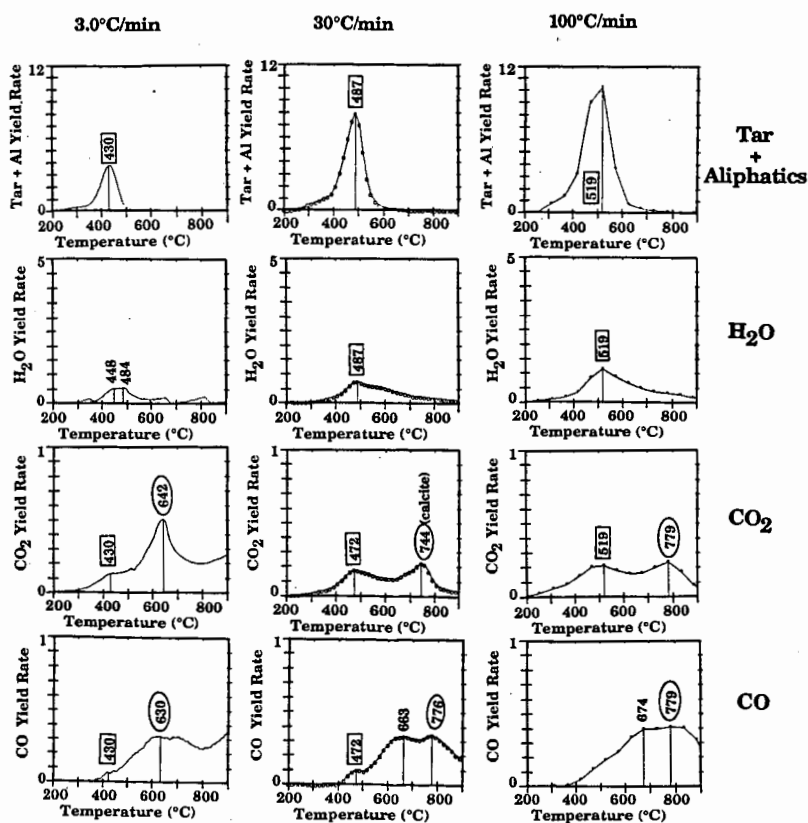


Figure 7. Evolution of Tar, H₂O, CO₂, and CO from Utah Blind Canyon Coal at Three Heating Rates.

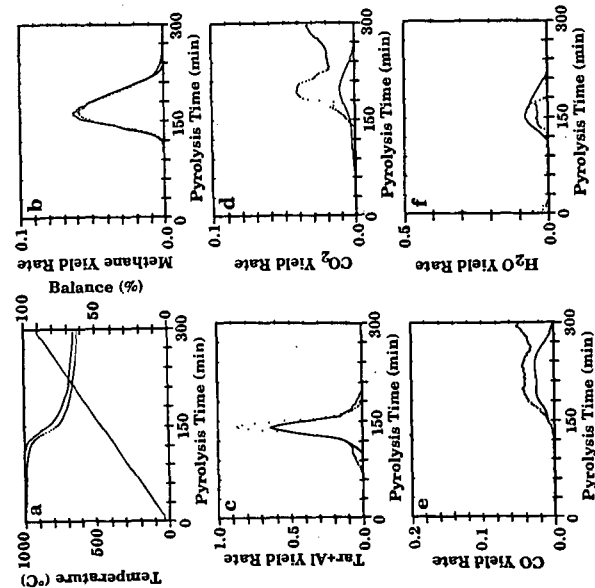


Figure 8. Data from TG-FTIR Heating Rates (---) and Predictions of FG-DVC Model for Pittsburgh No. 8 Bituminous Coal at 3°C/min. a) Weight Loss and Temperature; b) Methane; c) Tar + Aliphatic Gases; d) CO₂; e) CO; f) H₂O.

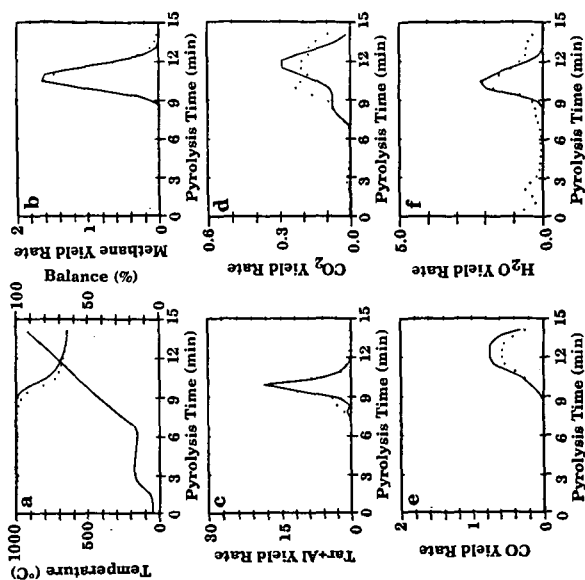


Figure 9. Data from TG-FTIR Heating Rates (---) and Predictions of FG-DVC Model for Pittsburgh No. 8 Bituminous Coal at 100°C/min. a) Weight Loss and Temperature; b) Methane; c) Tar + Aliphatic Gases; d) CO₂; e) CO; f) H₂O.